

FINAL REPORT
U. S. Department of Energy

Removal of Radioactive Cations and Anions from Polluted Water Using
Ligand-Modified Colloid-Enhanced Ultrafiltration (60041-OK)

Lead Principal Investigator:

Dr. John F. Scamehorn
Asahi Glass Chair
University of Oklahoma
School of Chemical Engineering and Materials Science
T335 Sarkeys Energy Center, 100 East Boyd St.
Norman, Oklahoma 73019
405-325-4382, scamehor@ou.edu

Co-Investigator:

Dr. Richard W. Taylor
University of Oklahoma
Department of Chemistry and Biochemistry
620 Parrington Oval
Norman, Oklahoma 73019
405-325-3820, rwtaylor@ou.edu

Co-Investigator at Lawrence Livermore National Laboratory:

Dr. Cynthia E. Palmer
Lawrence Livermore National Laboratory
P.O. Box 808
Livermore, California 94550
510-422-5693, palmer2@llnl.gov

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3. EXECUTIVE SUMMARY

The purpose of this project was to develop, optimize, and evaluate new separation methods for removal of hazardous (radionuclides and toxic non-radioactive contaminants) metal ions from either ground water or aqueous waste solutions produced during Decontamination and Decommissioning operations at DOE sites. Separation and concentration of the target ions will result in a substantial reduction in the volume of material requiring disposal or long-term storage. The target metal ions studied were uranium, thorium, lead, cadmium, and mercury along with chromium (as chromate). The methods tested use membrane ultrafiltration in conjunction with water-soluble polymers or surfactants with added metal-selective chelating agents. Laboratory scale tests showed removal of 99.0-99.9% of each metal tested in a single separation stage.

The methods developed for selective removal of radionuclides (UO_2^{2+} , Th^{4+}) and toxic heavy metals (Pb^{2+} , Cd^{2+} , Hg^{2+}) are applicable to two DOE focus areas; decontamination of sites and equipment, and in remediation of contaminated groundwater. Colloid-enhanced ultrafiltration methods have potential to be substantially less expensive than alternative methods and can result in less waste. Results of studies with varying solution composition (concentration, acidity) and filtration parameters (pressure, flow rate) have increased our understanding of the fundamental processes that control the metal ion separation and colloid recovery steps of the overall process. Further laboratory studies are needed to improve the ligand/colloid recovery step and field demonstration of the technology is needed to prove the applicability of the integrated process. A number of graduate students, post-doctoral associates, and research associates have received training and research experience in the areas of separation science, colloid chemistry, and metal ion coordination chemistry of radionuclides and toxic metals. These scientists, some with

positions in industry and academia, have the necessary background to address problems related to environmental remediation and management. The results of this research show the technical feasibility of this separation technique to concentrate radionuclides and toxic metals. The technology developed during this project has wider applications and has been studied for removal of chromate or chlorinated phenolics from industrial wastewater. In several cases, field tests have shown that using colloid-based ultrafiltration is feasible on real-world polluted waters.

The project involved collaboration between the University of Oklahoma and Lawrence Livermore National Laboratory. Research involving enriched radionuclides was carried out at Lawrence Livermore and most of the ultrafiltration was carried out at the University of Oklahoma. This permitted technology transfer between the two laboratories: techniques to work with radionuclides learned from Lawrence Livermore National Lab and colloid-enhanced ultrafiltration techniques from University of Oklahoma.

4. RESEARCH OBJECTIVES

The project was conducted to determine the feasibility of and develop optimum conditions for the use of ligand-modified colloid-enhanced ultrafiltration (LM-CEUF) methods to remove and recover radionuclides and associated toxic non-radioactive contaminants from polluted water. The target metal ions in this study were uranium, thorium, plutonium, strontium, lead, and cadmium along with chromium (as chromate). Several anionic or amphiphilic chelating agents, used to confer the selectivity required for removal of the target cations, were evaluated. Acid stripping and precipitation were evaluated as downstream methods separate the pollutants from the colloids and ligands and to concentrate the contaminants for disposal and permit recycle of the colloid for reuse. This project entailed a comprehensive study of the effects of solution composition and filtration unit operating parameters on the separation efficiency, ligand selectivity, and colloid/ligand recovery of LM-CEUF processes. This project addressed several areas of need identified by the Office of Environmental Management Science Program. These problem areas include removal of hazardous ionic materials from ground water, mixed waste, and aqueous waste solutions produced during Decontamination and Decommissioning (DDFA) operations. The methodology is also applicable to remediation of Subsurface Contamination (SCFA). Separation and concentration of the target ions will result in a substantial reduction in the volume of the material requiring disposal or long term storage. The research supported by this project expands the pioneering work in this area carried out at the University of Oklahoma on colloid-based ultrafiltration separations [1-9]. These new separation techniques allow selective removal of target ions in a single-phase continuous process and have the potential to remove pollutant cations and anions simultaneously. Recently other groups have reported applications of LM-CEUF for removal of radionuclides and toxic metal ions using surfactant micelles as the colloidal phase [10-16]. This research project was done in collaboration with workers at the Lawrence Livermore National Laboratory Laboratory where studies involving enriched radionuclides were carried out.

5. METHODS AND RESULTS

The research program involved a comprehensive study of the use of colloid-enhanced ultrafiltration processes (CEUF) to remove and recover the common radionuclide ions and other toxic metal ions from contaminated water. The simplest of these techniques involves the addition of either a water-soluble polyelectrolyte (PEUF) or micelle forming surfactant (MEUF) as the colloidal phase to the contaminated waste water. Subsequent ultrafiltration produces purified water and a homogeneous aqueous solution containing the concentrated pollutants and colloid. The ultrafiltration process is shown in schematic form in Figure 1(A). Downstream methods are used to separate the pollutants from the colloids, concentrate the contaminants for disposal, and recycle the colloids and added ligands for reuse in the process. When cationic polyelectrolytes or surfactants are used MEUF and PEUF remove ions of the same charge (e.g., Cu^{2+} , Ca^{2+} , Ni^{2+}) with approximately the same efficiency. In order to impart selectivity to the process, we used a method known collectively as ligand-modified colloid-enhanced ultrafiltration (LM-CEUF) which is shown in schematic form in Figure 1(B).

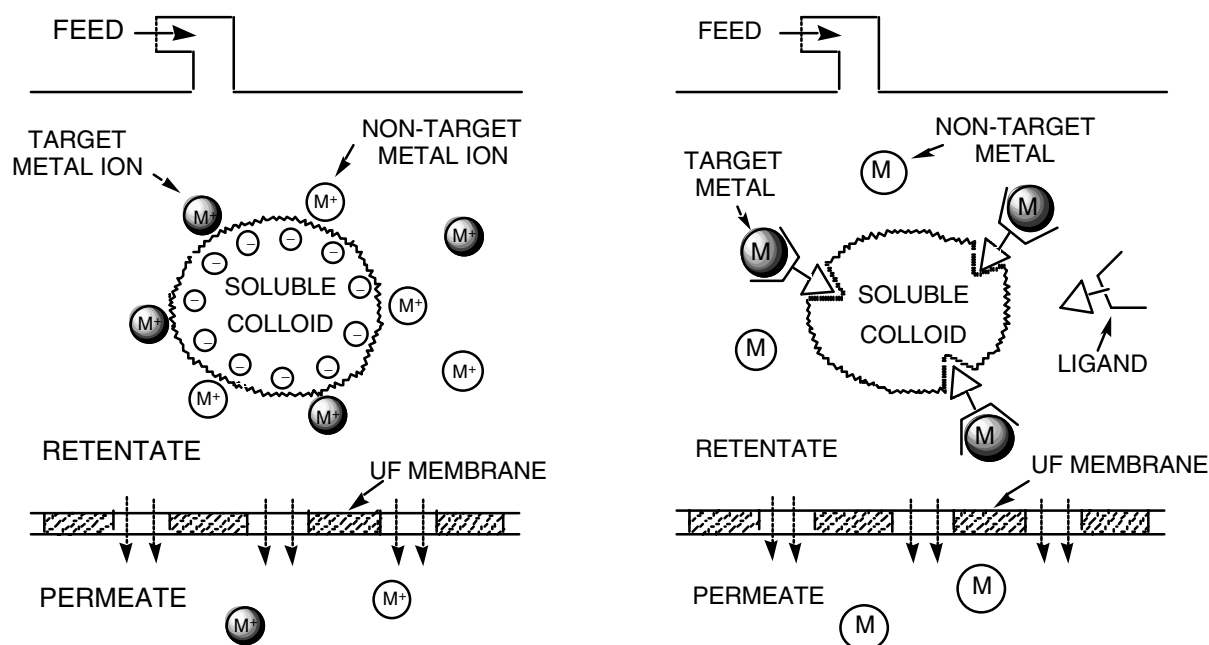


Figure 1. Schematic representation of the CEUF (A) and LM-CEUF (B) processes.

For LM-CEUF the added ligands contained a chelating polar head group chosen or designed to have high selectivity for the target ion. With LM-MEUF a long hydrocarbon tail was attached so that the ligand, and resulting complex, would solubilize strongly into the micelles. In LM-PEUF, anionic ligands were employed so that the free ligands and the resulting complexes had sufficient negative charge to bind to the colloidal polyelectrolyte by electrostatic interactions. For each method cationic (or neutral) surfactants or cationic polyelectrolytes were used so that non-target cations would not bind to the colloid. In the LM-MEUF method the colloidal phase was a surfactant at a concentration well above the critical micelle concentration (CMC), so that most of the surfactant is present as micelles. The vast majority of the ligand with the complexed target ions is then solubilized into the micellar phase or bound to the polyelectrolyte. The colloidal phase, containing the associated target species, is then removed by ultrafiltration using 5,000 to 10,000 molecular weight cutoff (MWCO) membranes. The extent of separation is expressed in terms of a rejection coefficient described by the following equation, where $[X]_{\text{per}}$ and $[X]_{\text{ret}}$ are

$$\text{Rejection} = (1 - [X]_{\text{per}} / [X]_{\text{ret}}) \times 100 \% \quad (1)$$

the concentrations of the target ion, X, in the permeate and retentate solutions, respectively. Early studies, using ligands synthesized in our laboratory as well as commercial products for removal of copper and lead from water, rejections of up to 99.2% have been observed [1-5,8,9] with no removal of calcium, indicating the high degree of selectivity and the high separation factor possible.

A limitation of LM-MEUF is that surfactant molecules are not entirely present as micelles. A low concentration of surfactant is present in monomeric form and passes through the membrane upon

ultrafiltration.[17,18] However, surfactant is required only when some organic material needs to be solubilized in the micellar interior. For the contaminated solutions of current interest the problem of monomer leakage can be eliminated by utilizing a water-soluble polyelectrolyte to replace the surfactant. This method (LM-PEUF) overcomes several weaknesses of previous techniques although use with solutions containing high levels of background electrolytes requires ligands/complexes with negative charge of at least -3 to offset the decreased electrostatic interaction. In fact, LM-MEUF and LM-PEUF provide alternate approaches for separations in the presence of high and low levels of background electrolyte. The use of LM-PEUF allows the simultaneous removal of target anions and cations, analogous to mixed bed ion exchange. After concentration of the colloids and target ions into a retentate stream by ultrafiltration, the colloid and ligand can be recovered by adjustment of pH or other means such as precipitation. A schematic diagram of the overall process is shown in Figure 2.

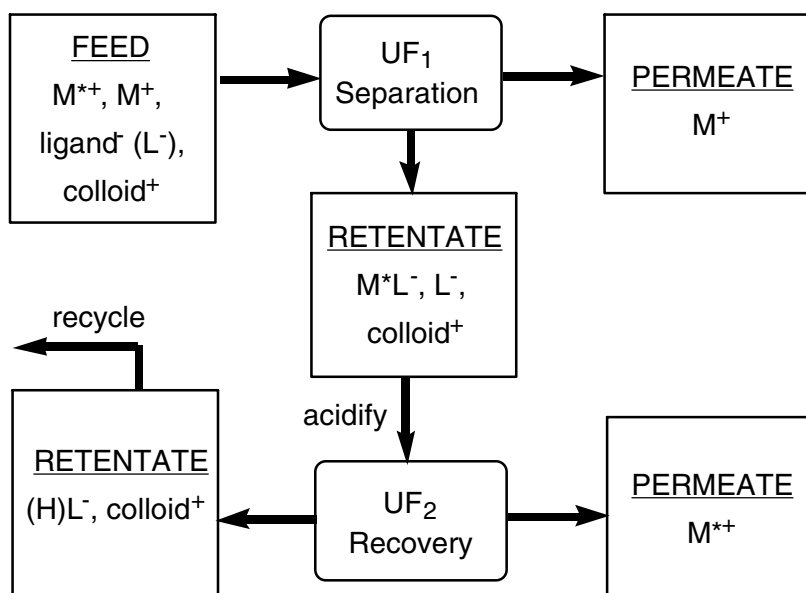
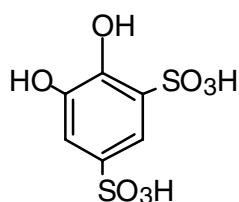


Figure 2. Schematic diagram of continuous two-stage ultrafiltration process for separation (UF_1) of target ions and recovery (UF_2) of colloid and ligands.

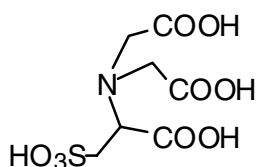
This project involved determining the efficiency and optimal operating conditions for this mixed ion removal process (e.g., selection of polyelectrolyte and ligand, maximum concentration of colloid during ultrafiltration). We used equilibrium dialysis methods for preliminary characterization of the separation/recovery performance. Once nominal operation conditions were established further studies used stirred-cell ultrafiltration units. We have carried out detailed studies to evaluate the effectiveness of the LM-CEUF method for a number of target metal ions and ligands. The metal ions include uranium (as UO_2^{2+}), lead (Pb^{2+}), thorium(IV), and cadmium (Cd^{2+}). In addition, preliminary results were obtained for a system designed to remove mercury (Hg^{2+}). A list of the ligands tested along with the target metal ions and types of colloids used is given below in Table 1 and the structures of the ligands (except carbonate) are shown in Figure 3.

Table 1. LM-CEUF systems studied.

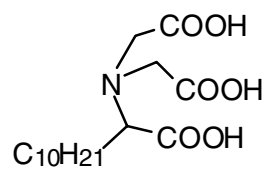
| Ligand (abbreviation) | Metal(s) | Colloid |
|---|---------------------------------------|---|
| carbonate (CO_3^{2-}) | UO_2^{2+} | cationic polyelectrolyte |
| dihydroxybenzenedisulfonic acid (DHBSA) | UO_2^{2+} , Th^{4+} | cationic polyelectrolyte |
| methylsulfonatonitrilotriacetic acid (SNTA) | Pb^{2+} | cationic polyelectrolyte |
| decylnitrilotriacetic acid (DN TA) | Pb^{2+} | cationic surfactant |
| undecyl-8-hydroxyquinoline (C_{11}HQ) | Cd^{2+} Cd^{2+} | cationic surfactant neutral surfactant |
| decylthiourea (DTU) | Hg^{2+} | cationic surfactant |



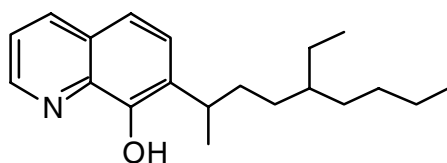
DHBSA



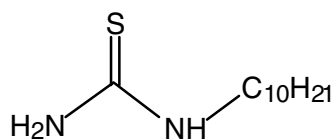
SNTA



DN TA



C_{11}HQ



DTU

Figure 3. Structures of ligands evaluated in this study

Although we focussed on LM-PEUF methods using a soluble cationic polymer as the colloidal phase, we have also investigated systems where surfactant micelles were employed in this capacity (LM-MEUF). We used polydiallyldimethylammonium chloride (PDADMAC) as the soluble cationic polyelectrolyte and cetylpyridinium nitrate (CPN) as the cationic surfactant. For one system (Cd^{2+} , C_{11}HQ) a neutral surfactant, hexaoxyethylene-*n*-dodecylether ($\text{C}_{12}(\text{EO})_6$), was also tested. The structures of the colloids used are shown in Figure 4.

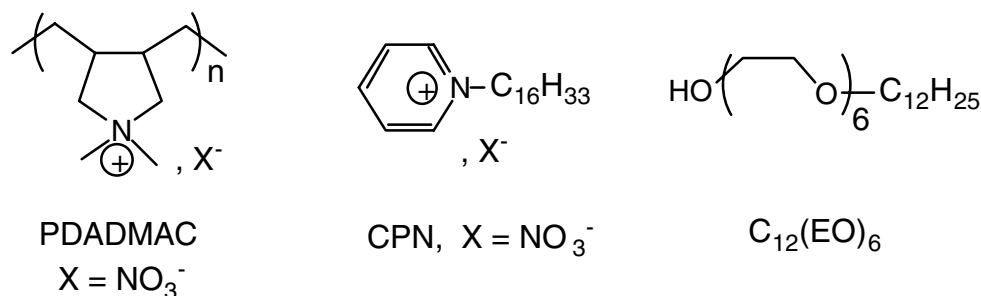
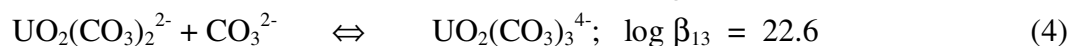
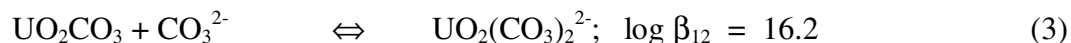
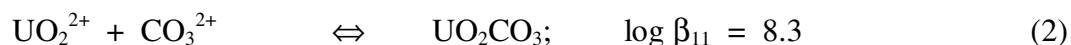


Figure 4. Structures of colloids used in LM-PEUF and LM-MEUF studies.

For each of the metal-ligand-colloid systems the separation efficiency, defined in terms of metal rejection (R_M (%); eq 1), was evaluated over a range of experimental conditions and various ultrafiltration cell operating parameters. The reaction conditions varied included the concentrations of metal, ligand and colloid solution, pH, and the presence of added electrolyte (salt). The effects of membrane pretreatment and applied pressure in UF experiments were also studied. Acid stripping and precipitation were investigated as potential processes for the recovery of ligands and colloid for recycling. Finally, tests were conducted to evaluate the potential of cyclic polyphenol compounds called calixarenes for use as ligands in LM-PEUF. The following sections describe in more detail the results for the individual systems and the implications for metal ion separations based on LM-CEUF.

Uranyl-carbonate

For removal of uranium in the form of uranyl ion, UO_2^{2+} , carbonate ion has several attractive properties as a ligand. It forms strong complexes with UO_2^{2+} where the higher order species have a net negative charge as shown by the following equilibria,



Formation of a trimeric $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ complex is reported to occur at high concentrations.[19] These polyanionic uranyl complexes would be suitable for removal using LM-PEUF. Furthermore, selectivity factors, defined as $\beta_{12}(\text{UO}_2)/\beta_{12}(\text{M})$ exceed 10^6 for most metal ions, the notable exceptions being NpO_2^+ ($\log \beta_{12} = 16.5$) and Hg^{2+} ($\log \beta_{12} = 14.5$). The former, along with PuO_2^{2+} which form stable carbonate complexes, are also potential target ions for LM-PEUF. Furthermore, carbonate (Na_2CO_3) is relatively inexpensive as a ligand. Finally, after separation from the feed solution, the $\text{UO}_2(\text{CO}_3)_n^{2-2n}$ complexes are easily dissociated by lowering the pH allowing removal of concentrated UO_2^{2+} for subsequent processing. We have carried out detailed studies for the $\text{UO}_2^{2+} - \text{CO}_3^{2-} - \text{PDADMAC}$ system using equilibrium dialysis and stirred-cell UF techniques over a wide range of experimental conditions. The factors examined included concentrations of UO_2^{2+} , CO_3^{2-} , PDADMAC, solution pH, presence of added salt, and applied pressure in the UF experiments. For the $\text{UO}_2^{2+} - \text{CO}_3^{2-}$ system at pH 7-8, solutions with

[CO₃]:[UO₂] total ratio greater than 4.0 gave $R_{UO_2} \geq 99.91\%$. This corresponds to UO₂²⁺ concentrations in the permeate as low as 0.1 µM, a reduction of about ~1000-fold in a single separation step. In the presence of 0.2 M or 0.5M NaCl the R_{UO_2} values decreased to ~95% and 80%, respectively, due to decreased electrostatic interaction. When the feed solution was adjusted to pH 2.4, uranyl rejection decreased to ~70%. Decreasing the applied pressure in the UF experiments from 60 to 30 psi resulted in a decrease in R_{UO_2} to ~45%. The role of pH, salt concentration and applied pressure on UF behavior will be investigated further as their combined effects may provide a suitable method to remove UO₂²⁺ and recycle the polymer.

Uranyl, thorium(IV) - dihydroxybenzenedisulfonic acid

Previous work from our laboratory showed that 1,2-dihydroxybenzenedisulfonic acid (DHBSA) was an effective ligand for LM-PEUF separations where Cu²⁺ or Pb²⁺ was the target ion.[4,5] Catechol ligands like DHBSA also form stable complexes with UO₂²⁺, Th⁴⁺ (and Pu⁴⁺) according to the following reactions,



For $M = UO_2^{2+}$, the net charges on the 1:1 and 1:2 complexes are -2 and -6, respectively; while for Th⁴⁺, the corresponding charges are 0 and -4, respectively. These properties, along with the high selectivity for the target ions, prompted us to evaluate DHBSA as a ligand for UO₂²⁺ and Th⁴⁺ in LM-PEUF. For both metal ions rejection exceeded 99.9% in the pH range 5.0-6.5 when the ligand:metal ratio was 2.0 or greater. The presence of the 0.2 M NaCl caused R_{UO_2} and R_{Th} to decrease slightly to 99.8% and 99.5%, respectively. Preliminary studies indicated that acid stripping at low pH (1-2) gave ligand recoveries of about 50%. The very high rejection values and the relative insensitivity to the presence of high concentrations of electrolyte, indicate that formation of the 1:2 complexes proceeds to a much greater extent (~ quantitative) than predicted from species distribution calculations using the available equilibrium constants in water. The presence of the cationic colloid shifts the equilibrium to favor the higher-order complexes with greater anionic charge.

Lead-nitrilotriacetic acid (NTA) derivatives

SNTA and DNTA (see Figure 3) were synthesized to test the behavior of a common chelating moiety (NTA) under LM-PEUF and LM-MEUF conditions, respectively. As noted previously, a potential problem with LM-PEUF is loss of ligand during UF in solutions with high levels of background electrolyte. The concentrations of Pb²⁺, ligand, background electrolyte, and colloid were varied as well as pH. Both ligands formed 1:1 complexes with Pb²⁺ in the presence of colloid. At low salt concentrations in the pH range 6 to 8 both ligands (L) provide excellent separation of Pb²⁺, with $R_{Pb} = 99.0-99.9\%$ for solutions with $[L]:[Pb^{2+}] > 1.0$. In the presence of 0.5 M NaCl rejection of Pb²⁺ decreases for SNTA-PDADMAC ($R_{Pb} = 50-55\%$) but remains essentially constant for DNTA-CPN, ($R_{Pb} = 99.5\%$). In the former case the electrostatic interaction between the anionic complex Pb(SNTA)²⁻ and the cationic polymer is diminished considerably by the presence of electrolytes. The decreased rejection was due to dissociation of the Pb(SNTA)²⁻ complex as analysis of the permeate solutions showed equal concentrations of

Pb^{2+} and SNTA, and, in the pH range studied (6-8) complex formation is almost quantitative. On the other hand, partition of the hydrophobic $\text{Pb}(\text{DNTA})^-$ complex into CPN micelles is hardly effected. In fact, in some studies rejection increased which may be due to a "salting in" effect for hydrophobic ligands in micelles. Acid stripping ($4 > \text{pH} > 3$) alone, or combined with precipitation of Pb^{2+} using auxiliary reagents (oxalate, sulfate) allowed removal of Pb^{2+} with ligand recoveries as high as 96% and 85% for SNTA and DNTA, respectively.

Cadmium-alkylhydroxyquinoline

An alkylated hydroxyquinoline was tested as a ligand for Cd^{2+} removal. The particular derivative studied, undecyl-8-hydroxyquinoline or C_{11}HQ (see Figure 3), is available as the commercial product "Kelex-100". The behavior of this ligand was studied using the cationic (CPN) or neutral ($\text{C}_{12}(\text{EO})_6$) surfactants as the colloidal phase. The values of the protonation constants (K_{Hi}) of the ligand (L) and the stoichiometry of the complexes were determined in both surfactants and for the parent compound in H_2O for comparison.



As found previously with other ligands [36], the protonation constants are shifted by 1-2 orders of magnitude compared to the underivatized parent compound 8-hydroxyquinoline. In the presence of the neutral surfactant $\text{C}_{12}(\text{EO})_6$ complexes with 1:2 CdL_2 stoichiometry predominate. However, with cationic CPN substantial amounts of 1:3 $(\text{Cd}(\text{L})_3)^-$ complexes are formed. This shift is a result of the favorable electrostatic interaction between the anionic 1:3 complex and the net positive charge on the CPN micelles. Similar behavior was apparent for the $\text{UO}_2\text{-CO}_3$, $\text{UO}_2\text{-DHBSA}$, and Th-CHBSA systems with the cationic polyelectrolyte PDADMAC. The Cd^{2+} rejection was studied as a function of $[\text{Cd}^{2+}]$, $[\text{C}_{11}\text{HQ}]$, and pH for both surfactants. Cadmium rejection reached maximal values in the range of 99.0 - 99.7% at pH ~8 with $\text{C}_{12}(\text{EO})_6$ and pH ~9 with CPN. The difference in pH is most likely due to electrostatic effects on ligand K_{Hi} values and repulsion of Cd^{2+} by CPN. Addition of 10 mM NaCl had no effect on rejection at pH 9 ($R_{\text{Cd}} = 99.5 - 99.6\%$) for both surfactants. As the pH values are lowered the Cd^{2+} is released and, in the case of CPN, expelled into the permeate is shown in Figure 5. This study illustrates that manipulation of system pH provides the basis for separating the target metal by UF at higher pH, followed by recovery of the ligand and colloid (and release at the target ion) by a second UF process at lower pH. These results also show that the separation and recovery processes can be carried out over a narrow range of moderate pH values (e.g., 5 to 9).

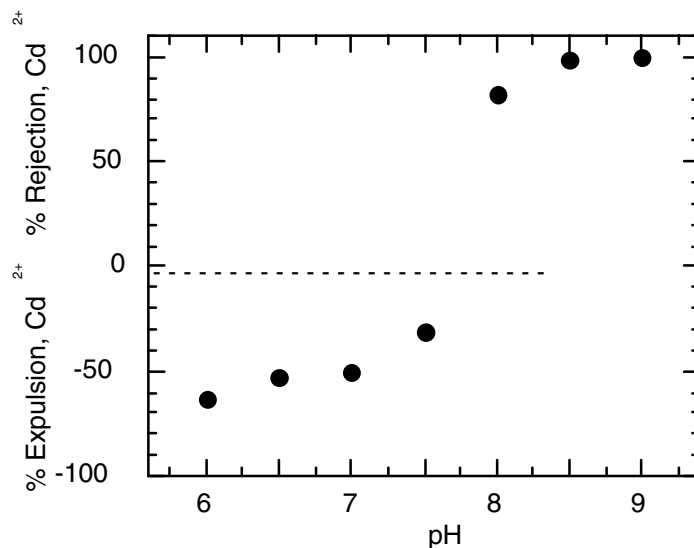


Figure 5. Rejection (eq 1) of Cd^{2+} as a function of pH for C_{11}HQ in CPN. Percent expulsion is defined as $E(\%) = (1 - [\text{Cd}^{2+}]_{\text{ret}} / [\text{Cd}^{2+}]_{\text{per}}) \times 100\%$.

Mercuric ion - decylthiourea

Thiourea (TU) forms strong complexes with Hg^{2+} with little interference from other metal ions except for Ag^+ and Pd^{2+} .^[20] Complexes with 1:2 Hg^{2+} / TU stoichiometry are favored although 1:3 and 1:4 complexes can form at high TU concentrations. The large magnitude of the overall complex formation constant (β_{12}) for the reaction,



allows almost quantitative complexation of Hg^{2+} for $\text{pH} < 8$. An equally attractive property of this ligand is the extremely high selectivity of thiourea compounds for Hg^{2+} . For example, the values of $\log \beta_{12}$ are all less than 2.2 for Co^{2+} , Cd^{2+} , Pb^{2+} , and Zn^{2+} . This gives selectivity factors, $S_{\text{Hg}/\text{M}} = \beta_{12}(\text{Hg}) / \beta_{12}(\text{M})$, of 10^{14} or greater for potentially competing metal ions (M). We carried out tests with Hg^{2+} using equilibrium dialysis methods using *n*-decylthiourea (DTU) as the ligand and CPN as the colloidal micellar phase. For pH values between 3 and 5, DTU forms predominately 1:2 Hg -DTU complexes. When the concentration ratio $[\text{DTU}]:[\text{Hg}^{2+}]$ was greater than 4:1 the rejection of Hg^{2+} was at least 99.8% in the pH range 3-5. The rejection values obtained for each metal ion / ligand / colloid system are summarized in Table 2.

Table 2. Rejection values for metal ion separations using LM-CEUF

| Metal ion | Ligand | Colloid | Rejection (%) |
|-----------|--------|---------|---------------|
|-----------|--------|---------|---------------|

| | | | |
|---------------------|---|-----------------------------------|---------------|
| UO_2^{2+} | carbonate (CO_3^{2-}) | PDADMAC | 96.1 – 99.98 |
| UO_2^{2+} | DHBSA (dihydroxybenzenesulfonate) | PDADMAC | 99.78 – 99.97 |
| Th(IV) | DHBSA (dihydroxybenzenesulfonate) | PDADMAC | 99.7 – 99.9 |
| Pb^{2+} | DNTA (decylnitrilotriacetic acid) | CPN | 99.4 – 99.9 |
| Pb^{2+} | SNTA (sulfonatnitrilotriacetic acid) | PDADMAC | 99.0 – 99.9 |
| Cd^{2+} | C_{11}HQ (undecyl-8-hydroxyquinoline) | CPN, $\text{C}_{12}(\text{EO})_6$ | 99.0 – 99.7 |
| Hg^{2+} | DTU (decylthiourea) | CPN | ≥ 99.8 |
| CrO_4^{2-} | none | PDADMAC | 99.0 – 99.7 |

Calixarenes

Calix[n]arenes are cyclic polyphenols generally consisting of 4 to 8 phenol moieties (n) joined by methylene bridges as shown in Figure 6.

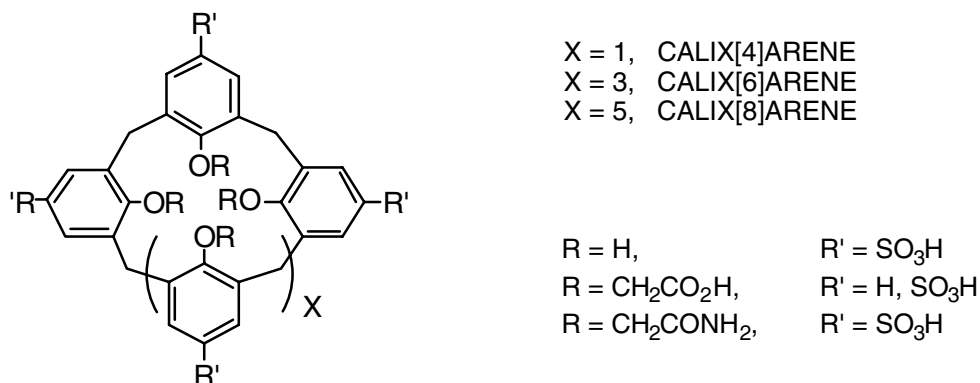


Figure 6. Structures of calix[n]arene type ligands.

The phenolic oxygens are readily derivatized to provide ligands with the appropriate number and type of donor atoms to match the coordination properties of the target ion.[21,22] For example, calix[6]arene derivatives can provide a planar hexagonal lattice of oxygen donors which matches the coordination geometry of UO_2^{2+} (hexagonal bipyramidal) giving rise to both high complexation strength ($\log \beta_{11} = 10^{17}$) and selectivity ($S_{\text{U/Cu}} > 10^{12}$).[23] Calixarene type ligands

have great potential for LM-CEUF based separations because the position opposite the phenolic oxygen also can be readily modified.[21,22] Sulfonic acid ($-\text{SO}_3\text{H}$, $\text{pK}_a \geq 1$) substituents can be introduced on each phenol ring at the 4-position giving ligands with a net ionic charge of -4 to -8 depending on the number of monomer repeat units. We synthesized the tetrasulfonate derivative of calix[4]arene and carried out UF studies with PDADMAC varying the added salt (NaCl) from 0.0 to 0.5 M to evaluate the effect of electrolyte concentration on retention of the ligand. The results of initial studies are shown below for solutions containing calix-[4]-arenetetrasulfonic acid (0.1 mM) and PDADMAC (5 mM).

| | | | | | |
|----------------------|--------|-------|-------|-------|-------|
| [NaCl], M | 0.0 | 0.1 | 0.2 | 0.3 | 0.5 |
| % R_{CALIX} | >99.95 | >99.9 | >99.9 | >99.9 | >99.8 |

Even at 0.5 M NaCl the rejection values are 99.8% or greater, which corresponds to ligand losses to the permeate of 0.2% or less. These results indicate that calix[n]arene polysulfonates can serve as the basic building block for ligands that could be used in LM-PEUF when there are high concentrations of background electrolytes.

6. RELEVANCE, IMPACT, AND TECHNOLOGY TRANSFER

a. How does this new scientific knowledge focus on critical DOE environmental management problems?

The techniques studied here provide an efficient way to concentrate target ions, while leaving the original water with a very low concentration of these ions. This is useful in **“Decontamination and Decommissioning”** of sites and equipment, and in remediation of **“Subsurface Contamination”**, two of the major **focus areas** identified by DOE in which a need to treat radioactive contaminants. In this study, selective removal of radioactive ions like uranium, as well as associated ionic pollutants like chromate and lead, from water were demonstrated under different conditions. Generally speaking, in surfactant-enhanced subsurface remediation to clean-up contaminated soil, use of ultrafiltration to concentrate the flush solution prior to reinjection is crucial to economical operation. Further advance of understanding of the ultrafiltration step in the presence of colloids pursued here help promote this process. The DOE has many sites in which this technique is needed to remove organic contaminants. This broadens the impact of this research beyond the groundwater aspects directly addressed here to soil remediation and to organic contaminants as well as ionic (radioactive and non-radioactive) species studied here.

b. How will the new scientific knowledge that is generated by this project improve technologies and cleanup approaches to significantly reduce future costs, schedules, and risks to meet DOE compliance requirements?

The innovative technique studied here utilizing colloids and ultrafiltration has potential to be substantially less expensive than alternative methods

c. To what extent does the new scientific knowledge bridge the gap between broad fundamental research that has wide ranging applications and the timeliness to meet needs-driven applied technology development?

The scientific knowledge gained in this study provides the basis for methods that address DOE problems. As noted in section (i), certain elements of the new technology have been scaled up to the field-test level.

d. What is the project's impact on individuals, laboratories, departments, and institutions?

This project has allowed continuing development of this innovative separation method, which permits us to use it for other important applications. For example, we have been able to study removal of chromate from plating operations wastewater and removal of chlorinated phenolics from pulp and paper industry wastewater.

A number of students, post-doctoral associates, and research associates have received training and research experience in the areas of separation science, colloid chemistry, and metal ion coordination chemistry of radionuclides and toxic metals. These scientists have the necessary background to contribute to solutions of problems related to environmental remediation or management.

e. Are large scale trials warranted?

The results of this research show the technical feasibility of this separation technique to concentrate radionuclides and toxic metals. Demonstration of this capability in large scale trials are warranted.

f. How have the scientific capabilities of collaborating scientists been improved?

Students who have worked on this project now have positions in industry and academia, where some are continuing research in this area. Researchers at the Lawrence Livermore Laboratory have been exposed to colloid-enhanced ultrafiltration as a separation method to apply to various pollutants. Researchers at the University of Oklahoma have been exposed to how to handle and study plutonium and other highly radioactive ions. So, the two organizations have learned from each other and improved each other's capabilities.

g. How has this research advanced our understanding in the area?

The equilibrium between radionuclides and other toxic ions with ligands and micelles has been further quantified and understood. The pH dependence of this equilibrium has dictated how well regeneration techniques can work. Ultrafiltration experiments have indicated the relative importance of equilibrium vs. transport considerations in the actual ultrafiltration step.

h. What additional scientific or other hurdles must be overcome before the results of this project can be successfully applied to DOE Environmental Management problems?

Regeneration of the ligand/colloid needs to be further studied in the lab. Demonstration of the technology in the field is needed to prove the applicability of the process.

i. Have any other government agencies or private enterprises expressed interest in the project?

A small environmental firm (Surbec ART) which specializes in subsurface remediation has expressed an interest in applying the method. We have written several proposals together with them (none successful so far) to scale-up the technique in the field. Small scale field tests were carried out at Elizabeth City Coast Guard Base in North Carolina using colloid-enhanced ultrafiltration to move chromate from groundwater and at Hill Air Force Base in Utah and at a Coast Guard facility in Traverse City, Michigan using ultrafiltration to remove organic matter from soils for surfactant recovery in soil remediation [24,25]. While not directly addressing radionuclides, these field tests have shown that colloid-based ultrafiltration is feasible on real-world polluted waters.

7. PROJECT PRODUCTIVITY

Did the project accomplish all of the proposed goals? If not, why not? Was the project on schedule? Was the work plan revised? If so describe revision.

The original budget request of \$554,847 (for OU) was decreased to \$422,219 at the time of the award. The subcontract budget for LLNL was maintained at \$116,778. The budget reduction (~24%) necessitated a decrease in the scope of the project. Studies involving Sr and Pu were placed on a lower priority because preliminary studies with other target ions (e.g., UO_2^{2+} , Th^{4+} , Pb^{2+}) showed promising results. Within the scope of the revised budget and workplan the project accomplished

8. PERSONNEL SUPPORTED / ASSOCIATED WITH RESEARCH PROJECT

John F. Scamehorn - PI
Richard W. Taylor - Co-PI
Cynthia E. Palmer - Co-PI (LLNL)
Edwin E. Tucker - Research Associate
Udeni Dharmawardana - Post-Doc
Napaporn Komesvarakul Graduate Student
Laura I. Haley - Graduate Student
Olga G. Ivanova - Graduate Student
Bo Tan - Graduate Student
Hua Liu - Graduate Student
Gary Smith - Graduate Student
Kendra Cox - Graduate Student

9. PUBLICATIONS

a: Articles published in peer-reviewed journals.

Sylwester, E. R., Allen, P. G. Dharmawardana, U. R., and Sutton, M.: "Structural Studies of Uranium and Thorium Complexes with 1,2-Dihydroxy-3,5-benzenedisulfonate (Tiron) at Low and Neutral pH by X-ray Absorption Spectroscopy". *Inorg. Chem.*, **40**, 283 (2001).

Roberts, B.L., Scamehorn, J.F., and Christian, S.D., "Micellar-Enhanced Ultrafiltration in a Spiral Wound Ultrafiltration Module and Comparison with Stirred Cell Performance", in *Surfactant-Based Separations: Science and Technology* (Scamehorn, J.F., and Harwell, J.H., Eds.), *ACS Symp. Ser.*, Vol. 740 (2000), p. 158.

Fillipi, B.R., Brant, L.W., Scamehorn, J.F., and Christian, S.D., "Use of Micellar-Enhanced Ultrafiltration at Low Surfactant Concentrations and with Anionic/Nonionic Surfactant Mixtures", *J. Colloid Interface Sci.*, **213**, 68 (1999).

Tangvijitsri, S., Soponvuttikul, C., Saiwan, C., and Scamehorn, J.F., "Polyelectrolyte-Enhanced Ultrafiltration of Chromate, Sulfate, and Nitrate", *Sep. Sci. Technol.*, In Press.

b: None

c: Two additional manuscripts to be submitted to peer-reviewed journals are in preparation.

10. INTERACTIONS

a: Participation/presentations at meetings, workshops, and conferences.

1. National and International Meetings:

R. W. Taylor, J. D. Roach, J. F. Scamehorn, E. E. Tucker and S. D. Christian: "Use of Nitrilotriacetic Acid Derivatives as Ligands for the Removal of Lead with Ligand-Modified Micellar-Enhanced Ultrafiltration." 215th National ACS Meeting, Dallas, TX, March 29, 1998.

Udeni Dharmawardana, Sherril D. Christian, Richard W. Taylor, Edwin E. Tucker, John F. Scamehorn, Cynthia E. A. Palmer, and Darleane C. Hoffman: "Selective Removal of U(VI) and Th(IV) Ions from Nuclear Waste by Ligand-Modified Polyelectrolyte-Enhanced Ultrafiltration Using 1,2-Dihydroxy-3,5-benzenedisulfonic Acid Ligand". 217th National ACS Meeting, Anaheim, CA, Mar. 21-25, 1999. Abstract I&EC 111.

Udeni Dharmawardana, Sherril D. Christian, Richard W. Taylor, John F. Scamehorn, Cynthia E. A. Palmer, and Darleane C. Hoffman: "Use of Carbonate and 1,2-Dihydroxy-3,5-benzenedisulfonic Acid for Removal of Th(IV) and U(VI) from Water with Ligand-Modified Polyelectrolyte-Enhanced Ultrafiltration". 218th National ACS Meeting, New Orleans, LA, Aug, 22-26. 1999. Abstract NUCL 110.

Laura I. Haley and Richard W. Taylor: "Complexation of DinitroBAPTA with Divalent Cations". 218th National ACS Meeting, New Orleans, LA, Aug, 22-26. 1999. Abstract INOR 405

Udeni Dharmawardana, Sherril D. Christian, Richard W. Taylor, John F. Scamehorn, Cynthia E. A. Palmer, Patrick G. Allen, Eric R. Sylwester, and Darleane C. Hoffman: "Selective Separation of Uranium (VI) and Thorium (IV) Ions by Ligand-Modified Polyelectrolyte-Enhanced Ultrafiltration Using 1,2-Dihydroxy-3,5-benzenedisulfonic Acid Ligand". 219th National ACS Meeting, San Francisco, CA, Mar. 26-30, 2000. Abstract NUCL 54.

Olga G. Ivanova, Warren L. Erdahl, Douglas R. Pfeiffer, and Richard W. Taylor: "Complexation of Lead(II) with the Polyether Ionophore Monensin", 219th National ACS Meeting, San Francisco, CA, Mar. 26-30, 2000. Abstract INOR 170.

P. Pookrod, Haller, K. J., and J. F. Scamehorn: "Removal of Arsenic Anions from Water using Polyelectrolyte-enhanced Ultrafiltration", 222nd ACS National Meeting, Chicago, August, 2001.

C. Soponvuttikul, C. Saiwan, and J. F. Scamehorn, "Use of Polyelectrolyte-Enhanced Ultrafiltration to Remove Chromate from Water-Polymer Recycle by Precipitation", 222nd ACS National Meeting, Chicago (August, 2001).

N. Komesvarakul, H. Gecol, and J. F. Scamehorn: "Purification of Phenolic-Laden Wastewater from Pulp and Paper Industry by Colloid-Enhanced Filtration", 92nd Annual AOCS Meeting, Minneapolis, May, 2001.

C. Soponvuttikul, C. Saiwan, and J. F. Scamehorn: "Recovery of Polyelectrolyte from Polyelectrolyte-Enhanced Ultrafiltration (PEUF) by Crystallization Process", Chemical and Process Engineering Conference (CPCE 2000), Singapore, December, 2000.

C. Soponvuttikul, C. Saiwan, and J. F. Scamehorn: "Recovery of Polyelectrolyte from Polyelectrolyte-Enhanced Ultrafiltration by Precipitation Process: Equilibrium Precipitation", 91st Annual AOCS Meeting, San Diego, April, 2000.

2. Department of Energy Workshops

R. W. Taylor, U. Dharmawardana, J. F. Scamehorn, E. E. Tucker and S. D. Christian: "Ligand-Modified Polyelectrolyte-Enhanced Ultrafiltration: Use of Carbonate and 1,2-Dihydroxy-3,5-benzenedisulfonic Acid to Remove UO_2^{2+} from Aqueous Solutions". 1st DOE-EMSP Workshop, Chicago, IL, July 27-30, 1998.

Richard W. Taylor, Udeni Dharmawardana, Edwin E. Tucker, Sherril D. Christian, and John F. Scamehorn: "Ligand-Modified Polyelectrolyte-Enhanced Ultrafiltration: Use of Carbonate and 1,2-Dihydroxy-3,5-benzenedisulfonic Acid to Remove UO_2^{2+} from Aqueous Solutions". DOE Environmental Management Science Program/Decontamination and Decommissioning Workshop, Nov. 15-18, 1998, Savannah River Site, Aiken, SC.

Udeni Dharmawardana, Jim D. Roach, Sherril D. Christian, John F. Scamehorn, Cynthia E. A. Palmer, Darleane C. Hoffman, and Richard W. Taylor: "Removal of Radioactive Cations and Anions from Polluted Water Using Ligand-Modified Colloid-Enhanced Ultrafiltration". 2nd National EMSP Workshop, Atlanta, GA, Apr, 24-27. 2000. Abstract B/O-III-24

Richard W. Taylor, John F. Scamehorn, and Cynthia E. A. Palmer: "Removal of Radioactive Cations and Anions from Polluted Water Using Ligand-Modified Colloid-Enhanced Ultrafiltration" 2nd National EMSP Workshop, Atlanta, GA, Apr, 24-27. 2000. Abstract 255.

b: Consultive and advisory functions to other laboratories and agencies

None

c: Collaborations

None (other than collaboration with Co-PI at LLNL)

11. TRANSITIONS

N/A

12. PATENTS

None

13. FUTURE WORK

Further laboratory studies of the regeneration step for recovery of the ligand and colloid are needed along with development of ligands selective for Sr and Pu. Demonstration of the technology in the field is needed to prove the applicability of the process. A proposal to extend this work was submitted to DOE-EMSP in April, 2001, but was not funded.

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15. FEEDBACK

N/A

16. APPENDICES

N/A